Gamma radiolytic stability of CyMe4BTBP and the effect of nitric acid

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Gamma radiolytic stability of $CyMe_4BTBP$ and the effect of nitric acid

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Abstract. The highly selective nitrogen donor ligand $CyMe_4BTBP$ for An(III) separation by solvent extraction was irradiated in a ^{60}Co γ-source under varying conditions. Organic solutions of 10 mmol/L ligand in 1-octanol were contacted with different concentrations of nitric acid to observe the influence of an aqueous phase during irradiation. In subsequent liquid-liquid extraction experiments, distribution ratios of ^{241}Am and ^{152}Eu were determined. Distribution ratios decreased with increasing absorbed dose when irradiation was performed in the absence of nitric acid. With addition of nitric acid, initial distribution ratios remained constant over the whole examined dose range up to 300 kGy. For qualitative determination of radiolysis products, HPLC-MS measurements were performed. The protective effect of nitric acid was confirmed, since in samples irradiated with acid contact, no degradation products were observed, but only addition products of the 1-octanol molecule to the $CyMe_4BTBP$ molecule.

Key words: $CyMe_4BTBP$ • gamma radiolysis • liquid-liquid extraction • nitric acid • partitioning • protective effect

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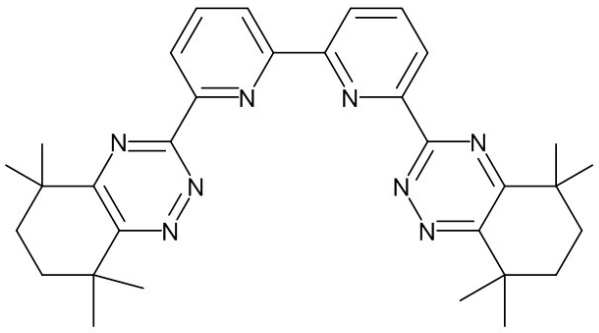
Introduction

Within international research in partitioning and transmutation (P&T), the separation of trivalent actinides (An(III)) from the chemical similar trivalent lanthanides (Ln(III)) is a main task that was comprehensively studied within the last two decades [1–3].

The investigated solvent extraction processes often follow the plutonium uranium reduction extraction (PUREX) process, in which uranium and plutonium are recycled from dissolved spent nuclear fuel solutions. For An(III) separation, a two-cycle concept, the so-called DIAMEX-SANEX concept, was developed [4]. In the first cycle the trivalent actinides were co-separated together with the lanthanides in the diamide extraction (DIAMEX) process [5, 6]. In the subsequent selective actinide extraction (SANEX) process, An(III) were selectively partitioned using the highly selective nitrogen donor ligand $CyMe_4BTBP$ (6,6′-bis(5,5,8,8-tetramethyl--5,6,7,8-tetrahydro-benzo[1,2,4]-triazin-3-yl)--[2,2′]-bipyridine) (Fig. 1) [7, 8]. A hot SANEX process demonstration was conducted using a genuine feed solution containing Ln(III) as well as Am(III) and Cm(III). Those An(III) were selectively extracted, whereas the lanthanides were routed to the raffinate stream [9]. In further work this SANEX process was modified to be able to extract the actinides directly from PUREX raffinate [10–12].



CyMe$_4$BTBP
6,6'-Bis(5,5,8,8-tetramethyl-
5,6,7,8-tetrahydro-benzo[1,2,4]-triazin-3-yl)
[2,2']-bipyridine

Fig. 1. Chemical structure of the CyMe$_4$BTBP ligand.

For the development of processes on an industrial scale, one main issue to consider is the detailed knowledge of radiolytic stability of the chemicals used since a solvent would be in contact for longer times with highly radioactive process streams. Degradation of the solvent may lead to the production of interfering degradation products, decreases in ligand concentration and changes in solvent viscosity as well as phase separation parameters [13]. This degradation may result in losses in selectivity and affinity for target metal extraction.

Radiolytic degradation of the BTBP ligand family was investigated previously [14–16]. A variety of different BTBP molecules was developed, such as C5-BTBP (6,6′-bis(5,6-dipentyl-[1,2,4]triazin-3-yl)-[2,2′]bipyridine) or the annulated MF2-BTBP (4-tert-butyl-6,6′-bis-(5,5,8,8-tetramethyl-5,6,7,8-tetrahydro-benzo[1,2,4]triazin-3-yl[2,2′]-bipyridine) and tested for their process performance [17]. Since it was proven that annulated BTBPs are much more stable towards radiolytic degradation than the tetra alkyl substituted BTBPs, those annulated systems were further investigated. Finally, the CyMe$_4$BTBP system was chosen as reference system in European research, resulting in the above mentioned SANEX process. Radiolytic stability of the SANEX solvent (CyMe$_4$BTBP + DMDOHEMA (*N*,*N*′-dimethyl-*N*,*N*′-dioctylhexylethoxymalonamide) in octanol) was studied by Magnusson *et al*. [18]. They investigated the radiolytic degradation for alpha as well as gamma radiation depending on the absorbed dose. The degradation of the extractant was found to be more severe for gamma radiolysis, as the reduction of distribution ratios was 40% higher compared to alpha radiolysis. This was explained by the higher LET of alpha radiation yielding in denser radiation tracks, allowing much faster recombination of radicals formed than in the case of gamma radiation [18].

The presence of an aqueous phase during irradiation of C5-BTBP in cyclohexanone was studied by Fermvik *et al*. [19]. It was found that in the presence of an aqueous phase the degradation of the extractant increased. A general review of the radiation chemistry of selective ligands for trivalent actinide recovery was published by Mincher *et al*. [20]. Sulich *et al*. examined the radiolysis of CyMe$_4$BTBP in 1-octanol pre-equilibrated with nitric acid using electron pulse radiolysis [21]. They added benzophenone and observed a protective effect on the ligand which was attributed to the addition of the aromatic ketone in higher concentration than the ligand, preferentially reacting with solvated electrons.

In this work, the radiolytic degradation of CyMe$_4$BTBP in 1-octanol and the influence of an aqueous phase in contact during irradiation were investigated. Experiments were conducted without an aqueous phase as well as in contact to different diluted nitric acid solutions.

Experimental part

CyMe$_4$BTBP was purchased from Technocomm Ltd., Falkland, United Kindom with a purity >98%. 1-Octanol (analytical grade, >99%) and concentrated nitric acid (65%, analytical grade) were purchased from Merck, Darmstadt, Germany.

Radiolysis experiments

Solutions of CyMe$_4$BTBP in 1-octanol (10 mmol/L) were irradiated either without contact to an aqueous phase or in contact to different diluted nitric acid solutions (0.1, 1.0 and 4.0 mol/L HNO_3). The irradiation was performed at the Department of Chemical and Biochemical Engineering at the Chalmers University of Technology in Gothenburg, Sweden. A ^{60}Co γ-source (Gammacell 220, Atomic Energy of Canada Ltd.) with a dose rate of ~9.5 kGy/h was used and samples were irradiated up to absorbed doses of 300 kGy. With increasing absorbed dose, the color of the former light yellow organic phase turned into a more reddish/orange color, which could indicate degradation of the pyridine moieties.

Liquid-liquid extraction

After removing the irradiated samples from the Gammacell, phases were separated (if necessary) and batch shaking experiments were performed. In each experiment 500 μL of the irradiated organic phase were contacted with 500 μL fresh 1.0 mol/L HNO_3 which was spiked with an ^{241}Am (1.6 kBq) and a ^{152}Eu (2.8 kBq) tracer. The samples were vigorously mixed for 90 min in a shaking device (2500 rpm) at 22°C and after centrifugation the phases were separated and aliquots of each phase were taken for analysis. Gamma spectroscopy was performed with a high-purity germanium detector obtained from EG&G Ortec, Munich, Germany and equipped with the Gamma Vision software. The gamma lines at 59.5 keV and 121.8 keV were analyzed for ^{241}Am and ^{152}Eu, respectively. The results are reported as distribution ratios D ($D = [M_{org}]/[M_{aq}]$), which have an uncertainty of ±5%, and where detection limits are $500 > D > 0.002$.

HPLC-MS experiments

MS measurements were performed using a Finnigan LCQ Fleet™ spherical Ion Trap LC/MS_n instrument (Thermo Scientific). All mass spectra were measured with APCI interface. 25 μL of the samples of initial concentration of the ligand were diluted to a volume of 1.0 mL with acetonitrile (for LC-MS, Aldrich, gradient grade). Mass spectra from direct infusion by a syringe were measured with APCI in positive mode. Conditions used for APCI interface: flow rate from a syringe infusion pump: 10 μL/min; sheath gas flow 15 L/min; auxiliary gas flow at 7 L/min, source voltage: 3.75 kV, vaporizer temperature 400°C; capillary temperature 250°C; capillary voltage 48 V, tube lens voltage 100 V and mass range from 50 to 2000.

Results and discussion

The radiolytic stability of $CyMe_4BTBP$ was first studied in the liquid-liquid extraction experiments using solvents irradiated to different doses up to 300 kGy. The irradiated samples were then analyzed by high-pressure liquid chromatography mass spectrometry (HPLC-MS) to determine the radiolysis products.

Liquid-liquid extraction experiments

Figure 2 shows the distribution ratios of ^{241}Am and ^{152}Eu as a function of absorbed dose for initially 10 mmol/L $CyMe_4BTBP$ in 1-octanol, when the organic phase was irradiated without contact to an aqueous phase. Both, the americium and europium distribution ratios decreased with increasing absorbed dose, in line with observations from Magnusson *et al*. [18] who used a mixture of $CyMe_4BTBP$ + DMDOHMA in octanol. Decreasing distribution ratios were observed up to an absorbed dose of 200 kGy (europium: 100 kGy), where the detection limit was reached. A linear decrease in distribution ratios was observed for europium (circles). For americium (squares), a delayed decrease in distribution ratios was found. After 75 kGy absorbed dose the slope of decreasing distribution ratios became steeper.

This could be explained by the formation of an intermediate species (see HPLC-MS section) that is also able to extract Am(III) to a certain amount, but is prone to radiolytic degradation with increasing dose itself. This behavior suggests there is no direct and exclusive degradation of the ligand by direct gamma irradiation alone but predominantly through indirect radiolysis [22–24]. It is well known, that during irradiation reactive radicals are formed mainly by radiolysis of the diluent, which can react with the extractant molecules (see discussion HPLC-MS, Eqs. (1)–(4)). Diluent molecules are present in much higher concentration than extractant molecules and are therefore more available for direct radiolysis.

The effect of nitric acid during irradiation was studied. Therefore, the organic solvent was irradiated in contact with different nitric acid concentrations from 0.1 to 4.0 mol/L HNO_3. For diluted 0.1 mol/L nitric acid, we could observe just slightly increased distribution ratios (Fig. 2). Irradiation experiments performed in contact with 1.0 mol/L nitric acid resulted in much higher distribution ratios. The observed distribution ratios did not decrease with increasing dose and the Am(III)/Eu(III) separation factor ($SF_{M1/M2} = D_{M1}/D_{M2}$) remained at the initial level with no observable changes (Fig. 3).

Obviously, the extracting system was protected by nitric acid against gamma radiation. The protection mechanism still needs to be resolved and in future experiments the individual influences of nitrate, acidity and water content will be studied. However, the added nitric acid seems to scavenge radicals built during radiolysis of the diluent. With increasing concentration of nitric acid from 0.1 mol/L to 1.0 mol/L, this scavenging became more effective until no reduction of distribution ratios was observed even at the highest doses studied here (300 kGy). Increase of the nitric acid concentration to 4.0 mol/L during irradiation

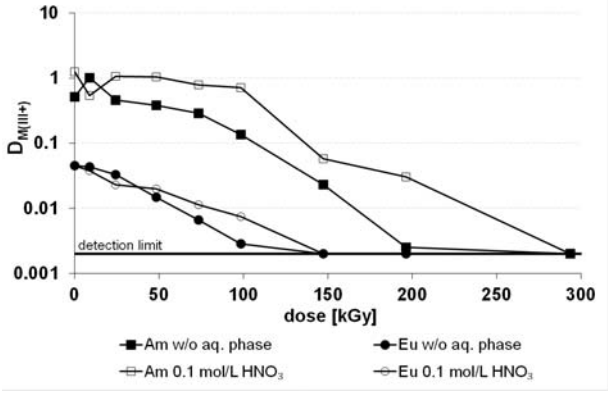


Fig. 2. ^{241}Am and ^{152}Eu distribution ratios of $CyMe_4BTBP$ irradiated without contact to an aqueous phase (closed symbols) and in contact with 0.1 mol/L nitric acid (open symbols) as a function of the absorbed dose. Organic phase: initially 0.01 mol/L ligand in 1-octanol, irradiated by ^{60}Co γ radiation, dose rate ~9.5 kGy/h. Aqueous phase: fresh 1 mol/L HNO_3, spiked with ^{241}Am and ^{152}Eu tracer; 90 min shaking time, 22°C.

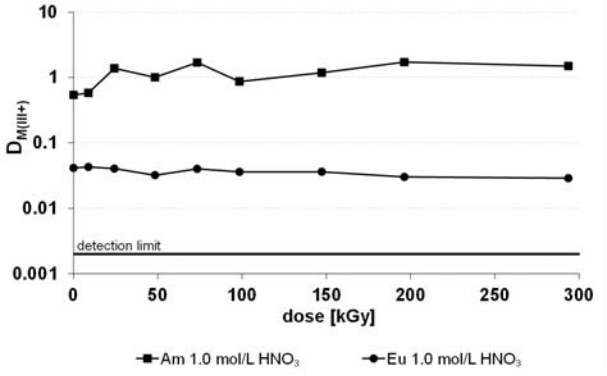


Fig. 3. ^{241}Am and ^{152}Eu distribution ratios of $CyMe_4BTBP$ irradiated in contact with 1.0 mol/L nitric acid as a function of the absorbed dose. Organic phase: initially 0.01 mol/L ligand in 1-octanol, irradiated by ^{60}Co γ radiation, dose rate ~9.5 kGy/h. Aqueous phase: fresh 1 mol/L HNO_3, spiked with ^{241}Am and ^{152}Eu tracer; 90 min shaking time, 22°C.

showed no further improvement. For clarification of the radiolysis mechanism HPLC-MS measurements were conducted to identify the radiolysis products and to investigate the influence of nitric acid addition on the radiolysis mechanism.

HPLC-MS analysis

Qualitative HPLC-MS analysis was performed to identify the radiolysis products of the gamma irradiated ligand solutions. Results of the liquid-liquid extraction studies suggest that there is at least one new species formed during irradiation in contact with nitric acid that is also able to extract the actinides. In neat samples (no irradiation, no contact to nitric acid, but prepared at the same time as the samples for irradiation) only the molecule peak was found m/z = (M + H^+) = 535.4 u. When irradiating the organic samples without contact to an aqueous phase, several different fragments were built with increasing yield towards increasing dose (Fig. 4). Products with heavier and lighter masses were detected suggesting also the degradation of extractant molecules.

In samples irradiated in contact with nitric acid, mainly one product was found with m/z = 663.4 u, which may be an addition product of one 1-octanol molecule to the $CyMe_4BTBP$ molecule. However, the HPLC-MS method does not give structural information. Lighter masses than the M + H^+ peak were only observed in negligible abundances.

The radiolysis of alcohols, such as isopropanol or hexanol, mainly results in the highly reactive α-hydroxy radicals as described in the literature by Eqs. (1)–(4) [25–29]. The reaction of diluent radicals with extractant molecules was reported as sensitization effect [30, 31].

(1) $$RCH_2OH + \rightarrow [RCH_2OH]^{\bullet}$$

(2) $$[RCH_2OH]^{*} \rightarrow e^{-} + [RCH_2OH]^{\bullet +}$$

(3) $$e^{-} \rightarrow e^{-}_{solv}$$

(4) $$[RCH_2OH]^{\bullet +} + RCH_2OH \rightarrow RC^{\bullet}HOH + RCH_2OH_2^{+}$$

According to this mechanism, it is very likely that during irradiation experiments, α-hydroxyoctyl

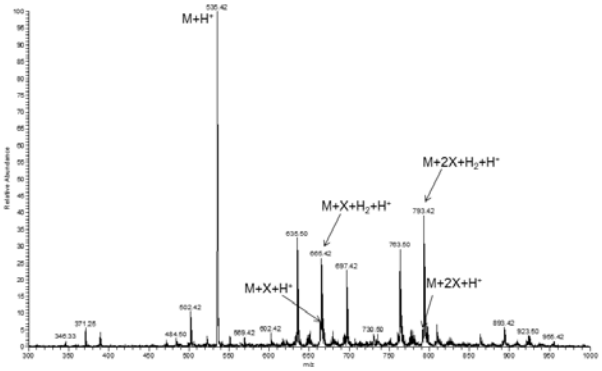


Fig. 4. $CyMe_4BTBP$ irradiated without contact to an aqueous phase to an absorbed dose of 100 kGy.

Table 1. Calculated mass to charge ratios for $CyMe_4BTBP$ and α-hydroxyoctyl adducts. (M = $CyMe_4BTBP$; X = α-hydroxyoctyl ($CH_3(CH_2)_6C^{\bullet}HOH$))

	Calculated m/z ratio	Molecular formula
M + H^+	535.33 u	$C_{32}H_{39}N_8^+$
M + X + H^+	663.45 u	$C_{40}H_{55}N_8O^+$
M + 2X + H^+	791.57 u	$C_{48}H_{71}N_8O_2^+$

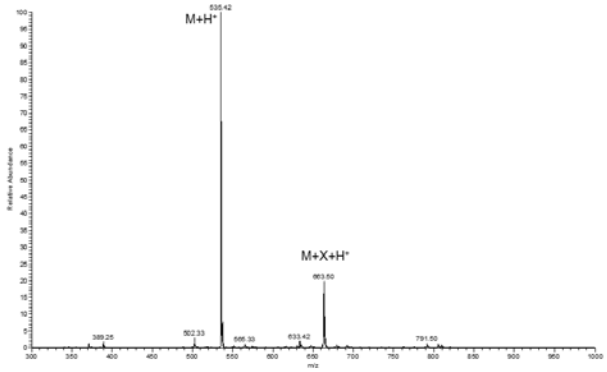


Fig. 5. $CyMe_4BTBP$ irradiated in contact to 1 mol/L HNO_3 to an absorbed dose of 100 kGy.

radicals were formed and reacted with the ligand molecule. This is in good agreement with the observed m/z ratios, especially in samples irradiated in contact with nitric acid, where exclusively M + X + H^+ (X = α-hydroxyoctyl ($CH_3(CH_2)_6C^{\bullet}HOH$)) was found (Table 1, Fig. 5). Based on the results from the liquid-liquid extraction, we assume that the reaction of the α-hydroxyoctyl is taking place on the 'periphery' of the ligand molecule. The tetradentate binding pocket made up by the nitrogen donor groups of $CyMe_4BTBP$, should not be occupied [32]. In the literature, radiolysis of nitric acid is well described and especially radical scavenging by HNO_3, NO_3^- or H^+ seems to be likely [33–40]. The individual influences of HNO_3, NO_3^- or H^+ will therefore be investigated and further detailed investigations of the radiolysis mechanism are planned (e.g. using pulse radiolysis). In samples irradiated without contact with an aqueous phase, also the higher addition product containing two α-hydroxyoctyl groups (M + 2X + H^+) was found (Fig. 4). The m/z ratio of this species is 791.75 which is present in the sample at a relatively low abundance. The dominating species is found to be M + 2X + H_2 +H^+ (m/z = 793.59). This observation is also true for the M + X product. This seems to be the product of the reduction of one of the double-bonds in the molecule.

Conclusions and outlook

The gamma radiolysis of the highly selective nitrogen donor ligand $CyMe_4BTBP$ was investigated in solution and the influence of nitric acid contact during irradiation was tested. A protection of $CyMe_4BTBP$ against radiolytic degradation was found for solutions irradiated in contact with nitric acid. In contrast to irradiation experiments without contact to nitric acid solutions, no decrease in ^{241}Am and ^{152}Eu distribu-

tion ratios was observed. As nitric acid is commonly used in partitioning processes for trivalent actinide separation, this protective effect plays a crucial role for the long-term performance of the used solvents.

A large number of radiolysis products was found in qualitative HPLC-MS measurements of samples irradiated without contact to an aqueous phase. In contrast, only the formation of 1-octanol adducts to the extractant was observed in samples irradiated in contact with nitric acid. The protective effect of nitric acid reduced the formation of other degradation products and the adducts are believed to potentially be able to extract trivalent actinides, as distribution ratios remained constant.

As the next step, it is planned to perform high resolution mass spectroscopy to further identify the radiolysis products and to synthesize 1-octanol adducts to $CyMe_4BTBP$. These synthesized molecules will then also be tested for their extraction abilities within the current European SACSESS project. Additionally, the $CyMe_4BTBP$ molecule, which is the current reference molecule in European research, will be compared to the very promising molecule $CyMe_4BTPhen$, where the bipyridine moiety is replaced by a phenanthroline functionality to fix the molecule in the *cis*-conformation resulting in a thermodynamically more favored metal-ligand complexation.

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